Feasibility of Subcritical Fluid Technology to Stabilize Archaeological Copper Alloy Artifacts

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Abstract

A PhD involving collaboration between Clemson University (USA) and Cardiff University (UK) is investigating the potential of subcritical fluid technology in the treatment of heritage copper alloys at the Warren Lasch Conservation Center. The work reported here examines the impact of temperature, pH and time on the chloride bearing compounds nantokite (CuCl), clinoatacamite[1] ($Cu_2(OH)_3Cl$) and atacamite ($Cu_2(OH)_3Cl$), of which the latter two are also referred to as trihydroxychlorides. These compounds were individually compressed into pellets, using calcium carbonate ($CaCO_3$) as a binder where necessary and subjected to continuous fixed flow of sodium carbonate (Na_2CO_3) 0.01 percent (w/w) (pH 10) and sodium bicarbonate ($NaHCO_3$) 0.00193 percent (w/w) (pH 8) solutions in subcritical conditions. Differing sample sets were run at 130°C, 180°C and 230°C for 1 and 5 hours. Eluate was sampled for chloride content at selected values of time. X-Ray diffraction and micro-Raman spectroscopy were used to investigate compound transformations that occurred during treatments. Nantokite and atacamite released significant amounts of chloride in all treatment environments. Varying degrees of transformation occurred for both compounds depending on parameters. Nantokite transformed to cuprite (Cu_2O) and copper trihydroxychloride ($Cu_2(OH)_3Cl$) while atacamite transformed to tenorite (CuO). Significant amounts of chloride detected in the eluate from clinoatacamite treatments could be assigned to residual sodium chloride (NaCl) from its synthesis as no compositional changes were detected, suggesting differing behavior from its polymorph atacamite. Hydrolysis of nantokite in high relative humidity produces atacamite and clinoatacamite, which physically disrupts patinas and alters the object aesthetics. Conversion to unreactive compounds in subcritical conditions offers the basis for developing a predictive evidence-based treatment option for the heritage sector.

Keywords

Subcritical fluid technology, high temperature, corrosion, desalination, archaeological copper alloys

Introduction

Copper alloy corrosion

Archaeological copper alloys form characteristic corrosion layers influenced by intrinsic factors within the alloy and the redox potential, pH, and water content of their burial environment. This often involves the highly mobile and soluble chloride (Cl^-) ion forming sparingly soluble nantokite (CuCl) at the metal surface, intermixed with copper (I) oxide (Cu_2O). Post-excavation high humidity (above 42 percent) and oxygen abundance may hydrolyze CuCl to produce mixtures of clinoatacamite ($Cu_2(OH)_3Cl$) and atacamite ($Cu_2(OH)_3Cl$). Their voluminous nature, formation and growth beneath overlying basic copper carbonate (malachite, azurite) and copper oxide (cuprite, tenorite) patinas lead to the physical destruction of these patinas and the evidence of original surface that they often contain, along with the object aesthetics. This reaction process is commonly termed 'bronze disease'. Attempts to prevent bronze

disease from occurring have utilized washing processes to remove chloride, CuCl reaction with silver oxide (Ag_2O) to form non-hydrolysable but visually displeasing silver chloride (AgCl) (Organ 1961, Sharma et al. 1995) and inhibition with benzotriazole. Transforming it to a more stable non-reactive corrosion product to release its chloride, which is then removed from the object, would be a beneficial treatment outcome.

Copper trihydroxychloride ($Cu_2(OH)_3Cl$) polymorphs are a symptom of post-excavation corrosion from CuCl hydrolysis and also the corrosion of copper in the presence of soluble chloride. Once formed, they offer no further risk beyond the physical damage they have already caused to patinas by their voluminous growth. They are insoluble and will not transform or release their chloride in any of the storage conditions expected in heritage contexts. As such they are symptomatic of corrosion rather than corrosion drivers and their removal will relate more to the needs of aesthetic goals.

Subcritical fluid technology

The subcritical setup is a closed system that utilizes a feed reservoir of deaerated treatment solution that is delivered to the specimen at a constant predetermined rate, thereby renewing wash solution and maintaining relevant concentration gradients (González-Pereyra et al. 2013). The specimen undergoing treatment is enclosed within a reactor cell, brought under pressure, and placed in a high temperature fluidized bath. The outflow containing solvated ions runs into the eluent receiver where its composition can be sampled for analysis. Subcritical aqueous solutions are maintained in a liquid state by heating under pressure between atmospheric boiling point at 100°C and their critical temperature of 374°C.

Decreased viscosity and density of solutions in subcritical conditions significantly improve penetration into the subsurface matrices of corroded iron and the reduced surface tension in subcritical conditions improves wetting. Solution polarity decrease occurs and produces enhanced solubility of otherwise insoluble or sparingly soluble compounds (Lu et al. 2001, Fernández-Prini et al. 2004, Kruse and Dinjus 2007), which releases anionic species for extraction. These factors reduce treatment time for chloride extraction, while retaining object metallography and the micro and macro structural integrity of corrosion product layers that relate to the concept of original surface.

Aim:

- to assess if subcritical washing of selected chloride-bearing copper compounds removes chloride from their structure and effects their transformation to other copper compounds that are chloride free.

Objectives:

- individually alkali-wash atacamite, clinoatacamite and nantokite in subcritical conditions using various pH, temperature and time options;
- determine whether subcritical treatment removes chloride from these compounds;
- analyze the treated compounds to detect if transformations have occurred.

Method

Subcritical treatment parameters

The controllable parameters of the subcritical system include the treatment solution, pressure, and temperature, pH of the treatment environment, flow rate and time. The goal here was to test wash solutions at pH 8 and pH 10 since copper, Cu_2O, CuO (Figure 1) and ($Cu_2(CO_3)(OH)_2$) stability fields exist within these pH ranges (Vink 1986, Beverskog and Puigdomenech 1995, Scott 2002, Stelzner and Eggert 2008) at the elevated temperatures of subcritical treatment. Therefore they may be expected to be the potential products of transformations.

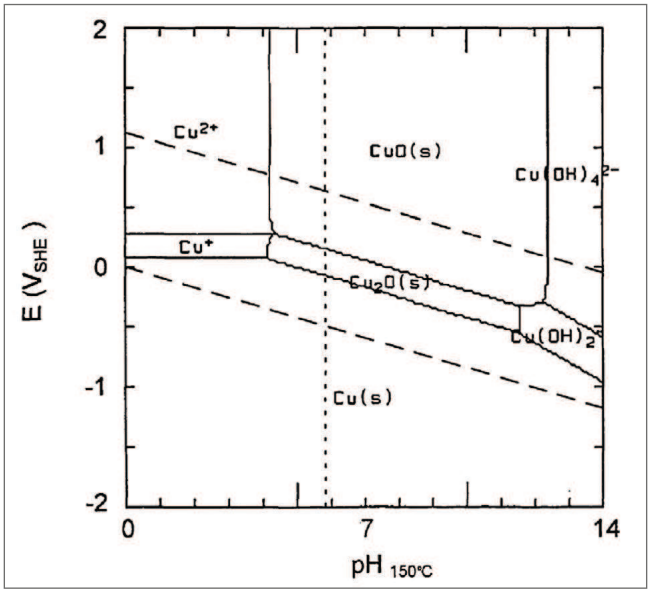

Figure 1. Potential/pH diagram of the copper water system at 150°C at atmospheric pressure and concentration of 10^{-4} m (Beverskog and Puigdomenech 1995)

Sodium carbonate (Na_2CO_3), at 0.01 percent (w/w) was selected for testing due to the dissociation constant (pKa) value of its conjugate acid being close to the upper pH limit of 10 from which it only deviates slightly. Sodium bicarbonate ($NaHCO_3$), at a concentration of 1.93 10^{-3} percent (w/w) was used to obtain pH 8. The sodium bicarbonate equilibrium reaction with water in a closed system is shown in equation (1).

$$CO_3^{2-} + H_3O^+ \rightleftharpoons HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \quad (1)$$

At elevated temperatures the endothermic reaction will absorb heat, causing the dynamic equilibrium to shift toward the right. This increases the number of hydroxide ions and the pH of the solution (Stefansson et al 2013), which is desirable for creating conditions that favor outward diffusion of chloride ions from the specimen and consequent transformations to copper oxides. Since the lower limit of the subcritical region is 100°C, the lowest temperature tested was 130°C and the upper limit was determined by the heater capability which is 250°C.

Sample production

Nantokite powder of 99 percent purity was purchased from Alfa Aesar. Atacamite and clinoatacamite were synthesized in the laboratory per Sharkey and Lewin, 1971. Atacamite synthesis involved placing 1.0 g of calcium carbonate ($CaCO_3$, S25220A[2] from Fisher Scientific) in 1 L of 1.0 M copper (II) chloride ($CuCl_2$ anhydrous 98 percent min powder from Alfa Aesar) solution and gently stirred for 4 h. The precipitate was separated by centrifuging and dried over 48 hours in a desiccator. Clinoatacamite was synthesized by dripping 100 mL of 1.0 M sodium hydroxide (NaOH, Macron Chemicals) into a solution of 1.0 M $CuCl_2$ accompanied by vigorous stirring. Once all the NaOH was used up, the mixture was decanted and centrifuged and the resulting solid oven dried at 60°C for 16 h and ground into a fine powder.

A 10-Ton, 13-mm hydraulic press (PIKE Technologies) was used to produce pellets of these compounds, using additives to provide cohesiveness for experimentation and analysis. A $CaCO_3$ (reagent grade S25220A from Fisher Scientific) binder was used for nantokite and atacamite to allow for better cohesion of the pressed pellets. Batches of these were produced after synthesis for atacamite, and as needed for nantokite, and stored in a desiccator at a relative humidity (RH) <20 percent before and after pressing into pellets. Homogenous pellets of thickness 1.5 mm ± 10 percent were produced. Powders and pressed pellets were weighed using Denver Instruments analytical balance (readable to 5 decimal points) and logged. The ratio of CuCl to $CaCO_3$ was 1:1 by mass and the mass range of the pellets was 0.79 g to 0.80 g. Similarly, a ratio of 1:1 by mass of atacamite to $CaCO_3$ was used to form the pellets and the mass range of the pellets was 0.59 to 0.60 g. The mass of clinoatacamite used to form the pellets ranged from 0.79 to 0.80 g. No binder was required for the formation of the clinoatacamite pellets.

Subcritical system

The subcritical reactor system comprised a feed solution reservoir (Nalgene bottle, style 2122 , size 4 L); high pressure digital pump (LabAlliance Series III); fluidized sand bath as a heat source and control (Techne SBL-2D with Eurotherm TC-8D); treatment cell (modified Swagelok SS-8F-60 12 mL internal volume stainless steel 316 filter housing); custom made 3-tier PTFE specimen rack (Industrial Netting); back pressure regulator (Tescom 1500 psi maximum regulated); and an eluate collection vessel. Laboratory grade sodium carbonate 0.01 percent (w/w) and sodium bicarbonate 0.00193 percent (w/w) treatment solutions were prepared daily in batches of 4 L using deionized water. Samples were placed on a Teflon rack in the reaction cell and the fluid flow path was primed to flush any air out of the system. The system was closed, pressurized to a set target of 50 bar, the cell introduced into the fluidized bath at a set temperature (130°C, 180°C or 230°C), and the flow stabilized. Solution flow rate was arbitrarily chosen as 1.5 mL/min for the 12 mL cell, which replaced the cell solution every 8 minutes. Temperature and pressure of the system were monitored using digital (Omega Engineering 0 to 2000 psig battery powered) and analogue (WIKA Type 232.53 Stainless Steel Industrial Gauge 0 to 2000 psi) gauges.

Table 1 indicates the combinations of run times, pH and temperature variables used in the experiments, as well as chloride concentration analysis times. Upon completion of the test run, the cell was extracted from the fluidized bath and the high-pressure cell cooled down by dousing the exterior with deionized water. The flow of eluent was allowed to continue throughout the cooling process. Once the cell reached room temperature, a brief rinsing cycle with deionized water as the eluent at a flow of 2.0 mL/min ran for a minimum of 15 minutes. The high-pressure

pump was turned off and the cell opened to retrieve the samples which were then placed on a glass slide and dried in an oven at 60°C for 20 minutes followed by storage at RH <20 percent.

Table 1. Treatment Parameters

Run time (min)	Eluent analysis intervals (min)	Sample			°C	pH
		Nantokite (N)	Atacamite (A)	Clino-atacamite (C)		
60	15; 30; 45; 60	1.1N	1.1A	1.1C	130	8
		1.2N	1.2A	1.2C		10
		1.3N	1.3A	1.3C	180	8
		1.4N	1.4A	1.4C		10
		1.5N	1.5A	1.5C	230	8
		1.6N	1.6A	1.6C		10
300	60; 120; 180; 240; 300	5.1N	5.1A	5.1C	130	8
		5.2N	5.2A	5.2C		10
		5.3N	5.3A	5.3C	180	8
		5.4N	5.4A	5.4C		10
		5.5N	5.5A	5.5C	230	8
		5.6N	5.6A	5.6C		10

Analytical protocol

Samples (5mL aliquots) were collected at the exit of the reactor cell to monitor chloride in the eluate at selected points in time. The pH of the aliquots taken was measured using Thermo Scientific Orion™ PerpHecT™ ROSS™ Combination pH Micro Electrode and neutralized to a pH range of 5.0 – 7.0 where required prior to chloride quantification. Chloride concentrations were measured with Quantab™ titrator strips (Hach). Both low range (30 to 600 ppm chloride) and high range (300 to 6000 ppm chloride) strips were used. A more precise chloride concentration was obtained by ion chromatography. Samples were diluted by weight and placed into Thermo Scientific 5 mL PolyVials with filter caps using a 1 mL syringe and 0.45 µm Nalgene Syringe Filters with PTFE membrane. Chloride concentrations were measured using a Thermo Scientific Dionex ICS-1100 ion chromatography system equipped with an Ionpac AS9-HC analytical column and coupled with a Dionex AS40 Automated Sampler. Spectra were analyzed using a two point calibration with the Dionex Chromeleon 7.0 software.

Dispersive µ-Raman spectroscopy (Bruker SENTERRA) was carried out for compound characterization before and after treatment. Spectra were produced using a 532 nm diode laser filtered to 5 mW, using a 50× bright field long working distance objective, a detector aperture of 50×1000 µm, with integration time of 30 seconds with 3 co-additions over a spectral range 70 to 3720 cm^{-1}. The OPUS Version 7.5 software was used for data collection and processing. Identification was performed by comparison to standards and available Raman databases (Bouchard and Smith 2002, Martens et al. 2003). Quantitative and qualitative elemental compositions were determined in select pellets by an Oxford INCAx-act analytical silicon drift energy dispersive spectrometer (EDS) fitted onto a Hitachi S-3700N Ultra Large variable pressure scanning electron microscope (VP-SEM). Data collected was analyzed with the INCAEnergy software interface. X-Ray fluorescence (XRF) with a Bruker handheld Tracer III-SD XRF spectrometer equipped with a vacuum using a blue filter (titanium) and 15 kV voltage and 55 µA anode current was employed for qualitative and semi-quantitative elemental analysis. XRD was carried out on samples sent to Bruker AXS Inc. where they were analyzed with a D8 ADVANCE diffractometer equipped with copper radiation (40 kV, 40 µA) and LYNXEYE XE-T detector (energy discriminating silicon strip detector). Diffraction samples were prepared using a low-background silicon wafer mount.

Results

X-ray diffraction data was collected for an atacamite pellet before subcritical treatment and the sample treated at 180°C for 5 hours at pH 10 (Figure 3, Table 2). For clinoatacamite an untreated pellet and the sample treated at 230°C for 5 hours at pH 10 are reported (Figure 4, Table 2). XRD was not available for nantokite characterization.

XRF analysis of atacamite (Figure 2) and clinoatacamite pellets provided semi-quantitative data on the change in chloride content at its surface (Table 3).

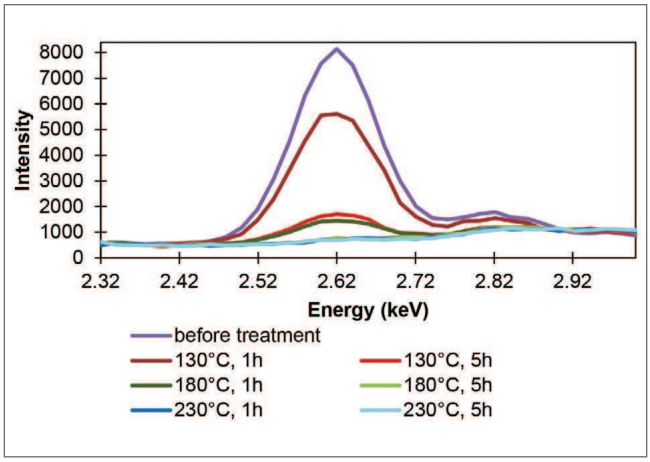

Figure 2. XRF spectra of chlorine in untreated and treated atacamite samples at pH 10

Table 2. Compounds in synthesized atacamite pellet before and after treatment at 180°C for 5 hours at pH 10 and for in clinoatacamite pellet before and after treatment at 230°C for 5 hours at pH 10. [1] See endnote for nomenclature

Sample	before treatment	PDF	after treatment	PDF
Atacamite pellet	$Cu_2Cl(OH)_3$ atacamite	04-013-1385	$Cu_2Cl(OH)_3$ atacamite	04-013-1385
	$CaCO_3$ calcite	00-005-0586	$CaCO_3$ calcite	00-005-0586
	$Cu_2Cl(OH)_3$ botallackite	04-011-8741		
	SiO_2 quartz	00-005-0490	SiO_2 quartz	00-005-0490
			CuO tenorite	04-007-1375
	$CaMg(CO_3)_2$ dolomite	04-008-0789	$CaMg(CO_3)_2$ dolomite	04-008-0789
Paratacamite Pellet[1]	$Cu_2Cl(OH)_3$ clinoatacamite	04-012-9781	$Cu_2Cl(OH)_3$ clinoatacamite	04-012-9781
	$Cu_2Cl(OH)_3$ atacamite	04-013-1385		
	NaCl halite	00-005-0628		

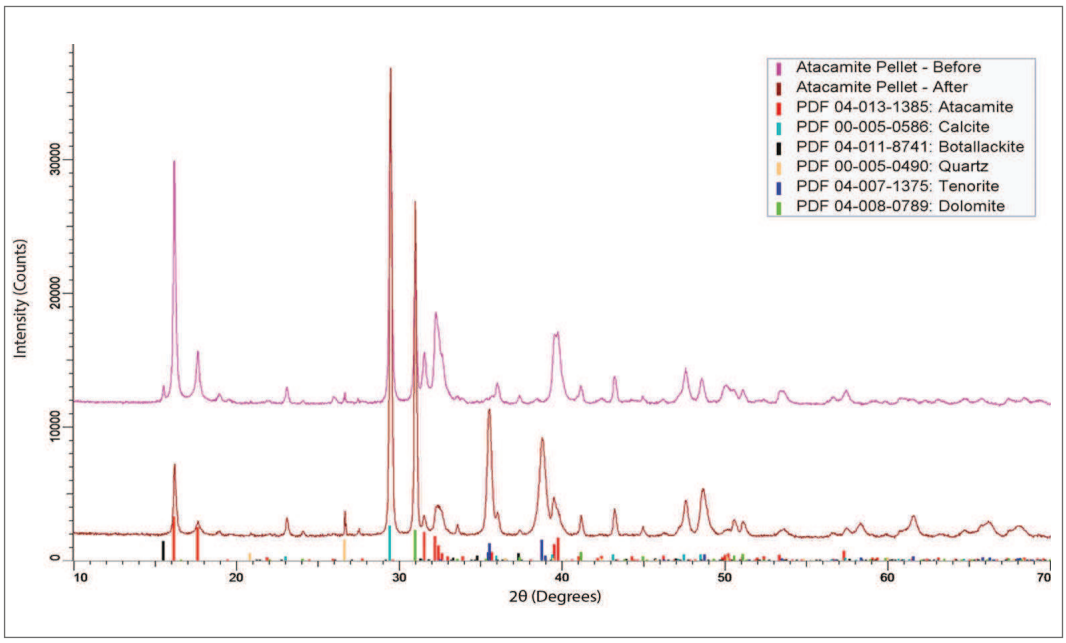

Figure 3. XRD spectra of atacamite pellet before and after subcritical treatment at 180°C pH 10 for 5 hours

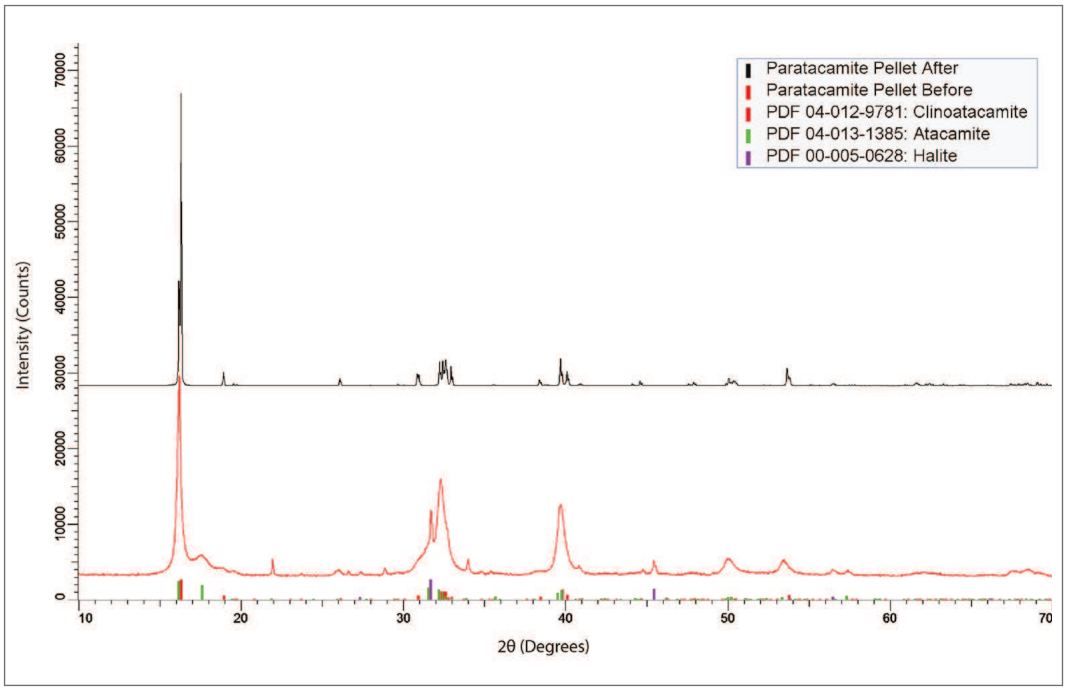

Figure 4. XRD spectra of clinoatacamite pellet before and after subcritical treatment at 230°C pH 10 for 5 hours

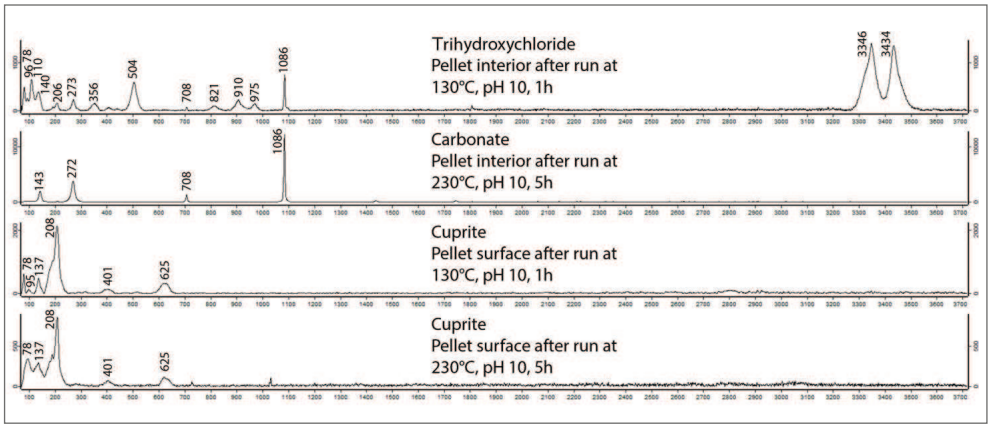

Figure 5. Micro-Raman spectra of the surface and interior of nantokite pellets treated at 130°C pH 10 for 1 hour and 230°C pH 10 for 5 hours

Table 3. Percentage decrease in chlorine at the surface of atacamite and clinoatacamite pellets calculated using XRF data

Parameters			Clinoatacamite % Change (decrease or increase)		Atacamite % Change (decrease or increase)	
°C	pH	Time (min)	Chlorine	Copper	Chlorine	Copper
130	8	60	-29.4	+0.34	-70.6	+4.66
		300	-41.3	+0.46	-91.4	+5.23
	10	60	-35.9	+0.38	-41.6	+1.72
		300	-42.4	+0.56	-86.9	+5.08
180	8	60	-43.3	+0.45	-91.2	+4.08
		300	-42.3	+0.33	-95.6	+3.67
	10	60	-43.0	-0.37	-91.6	+0.79
		300	-45.6	-0.69	-96.2	+5.35
230	8	60	–	–	-95.4	+4.04
		300	-50.6	-0.33	–	–
	10	60	-42.0	-0.07	-96.2	+4.91
		300	-46.5	+0.07	-96.6	+6.12

Micro-Raman spectra of the surface and interior of nantokite pellets treated at 130°C pH 10 over 1 hour and 230°C pH 10 over 5 hours were recorded (Figure 5).

Chloride concentration (ppm) in the subcritical eluate at t = x for atacamite, clinoatacamite and nantokite are recorded in Figures 6, 7 and 8.

Discussion

Subcritical treatment of nantokite, atacamite and clinoatacamite for 60 minute intervals showed a similar generic pattern of chloride release at all the operational pH and temperature values tested. The highest concentrations of chloride were recorded in the first 30 minutes (Figures 6A, 7A and 8A). A similar pattern emerged for the 300 minute treatments at all temperatures and pH values with the first reading, measured at the 60 minute interval, recording the highest chloride concentration (Figures 6B, 7B and 8B). Although the samples were

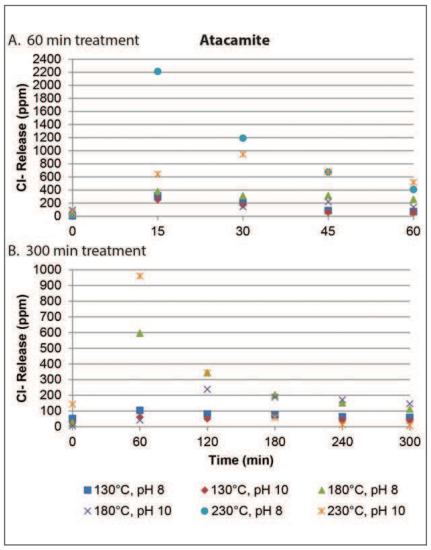

Figure 6. Chloride concentration in eluate for atacamite samples

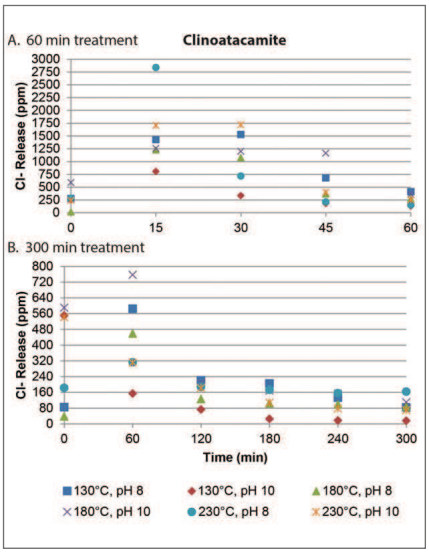

Figure 7. Chloride concentration in eluate for clinoatacamite samples

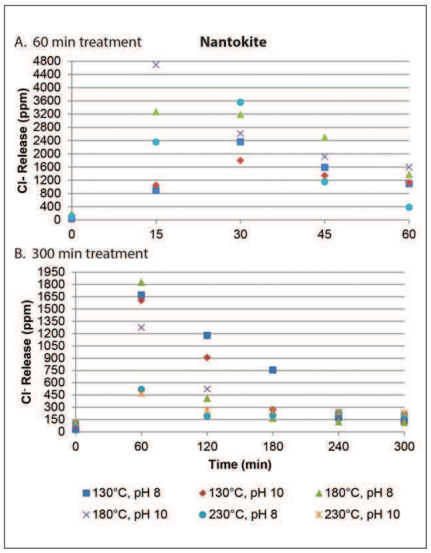

Figure 8. Chloride concentration in eluate for nantokite samples

consistent in terms of weight of the pellets, there was no reproducibility of chloride concentration in eluate for the data sets. The nantokite sample at 180°C pH 10 the final chloride concentration of the 60-minute treatment is 1650 ppm but for the same operational conditions the 300-minute treatment returned 1273 ppm at the 60-minute interval (Figure 8). The same is true for clinoatacamite and atacamite samples at the 60-minute sampling interval: clinoatacamite 180°C, pH 10, 400 ppm (60-minute treatment) 750 ppm (300-minute treatment) (Figure 7); atacamite 180°C pH 10 137 ppm (60-minute treatment) 30 ppm (300-minute treatment) (Figure 6). This could be due to a number of factors such as uneven mixing of pellet media and test compound, differential penetration of the pellets by the wash solution to access chloride and uneven outward diffusion of chloride, as well as morphology changes like cracking of pellets during treatment.

Both nantokite and clinoatacamite demonstrate higher concentrations of chlorine in their eluate as compared to atacamite. This could relate to the amount of total chlorine in the mass of the compound used to make up the pellets. There are 0.0040 mol of chlorine per pellet of nantokite and 0.0037 mol chlorine in clinoatacamite (disregarding amount of NaCl present), while there are only 0.0014 mol of chlorine in atacamite. Measuring the chloride extracted offers a guide to the rate of extraction but not the amount of chloride remaining or removed.

The high chloride release from the clinoatacamite can be partially attributed to the contamination with NaCl from the synthesis as determined with XRD (Figure 4, Table 2). While SEM EDS analysis indicates significant loss of chloride from the surface of the pellet, the post-treatment composition indicates that clinoatacamite is still present (Figure 4). In future synthesis, clinoatacamite will be washed with deionized water to remove NaCl impurities. In contrast atacamite shows some conversion to tenorite, CuO (Figure 3, Table 2). Tenorite is thermodynamically stable at the pH and temperature tested. The dolomite ($CaMg(CO_3)_2$) and calcite ($CaCO_3$) are present from the binder. Botallackite ($Cu_2Cl(OH)_3$) occurred as a byproduct from the atacamite synthesis and is no longer present in the pellet after treatment. At 130°C the nantokite pellet shows transformation to cuprite at its surface and trihydroxychloride within its interior, whereas at 230°C the latter could not be detected within the pellet interior (Figure 5).

Table 4. Molar volumes (m^3/mol) and color of selected copper corrosion products.

Compound	Molar Volume (m^3/mol)	Color
Nantokite CuCl	25.19	Light green
Tenorite CuO	12.24	Lustrous black/dark grey
Cuprite Cu_2O	23.46	Burgundy/dark red
Atacamite $Cu_2(OH)_3Cl$	56.65	Greenish blue/green
Clinoatacamite $Cu_2(OH)3Cl$	56.65	Greenish blue/green
Copper Cu	7.10	Reddish brown

Further examination is required before subcritical treatment can be considered a viable treatment option. The treatment time required for full conversion of chloride bearing compounds needs to be determined, particularly as nantokite is commonly found at the metal/corrosion product interface. The results are promising as they show both extraction of chloride and transformation of nantokite to more stable compounds, such as cuprite and trihydroxychloride, which will reduce reactivity of objects containing it. However, transformations to compounds of differing density produce volume changes that may be problematic (Table 4). Patinas may be disrupted, crack and become increasingly fragile and/or porous. Color change may be a consideration for aesthetic value, an issue remaining open to debate (Table 4).

Conclusion

The work presented reveals that all subcritical treatment conditions tested here are capable of total or partial transformation of the chloride bearing compounds nantokite and atacamite to non-chloride bearing products, such as cuprite and tenorite respectively, thereby releasing their chloride. Clinoatacamite, responding differently to treatment than atacamite, did not transform to non-chloride bearing compounds, which may be attributed to the NaCl impurity produced during synthesis. Within an object which exhibits corrosion, chemical stability will improve with removal of nantokite, prone to hydrolysis at high humidity. Subcritical treatment parameters require further investigation to identify operational values that will ensure complete transformation of nantokite, rather than the partial transformation observed at lower operating temperatures. Treatment limitations may occur

from color change produced by transformations and molar volume differences, which may impact aesthetics and physical integrity of patinas. These factors require investigation before the value of subcritical treatment can be determined.

Acknowledgements

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Endnotes

1 Pellet samples were labeled 'paratacamite' per nomenclature in Sharkey and Lewin 1971. The authors recognize the change in nomenclature thereafter, and the compound in question shall be referred to as 'clinoatacamite' throughout the work presented.

2 All chemicals used were reagent grade, unless otherwise specified.

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